

Geochemical approach to estimate the quality of water entering abandoned underground coalmines

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Abstract Geochemical modeling was employed to estimate the chemistry of water infiltrating into abandoned underground flooded and unflooded coalmines of the Uniontown syncline, Fayette County, Pennsylvania. This was done to help evaluate factors governing the long-term evolution of coalmine discharge water quality in the Uniontown syncline area. The subsurface structure and lithology was delineated using borehole, mine shaft, and stratigraphic information. Hydrogeologic analyses indicated that most of the recharge to mine voids occurs in the zones of shallow overburden cover of less than 20 m in thickness. The water–rock contact period in the recharge areas of the overburden was estimated to be 5 days or greater for the flooded mines, and a day or less for the unflooded mines. Flow-through reaction-path models were applied to the topsoil and shale–sandstone lithological units identified in the recharge areas. The model predicted water entering the flooded mines at a pH of 6.65, alkalinity of 6.92 mequiv. l^{-1} and a total sulfate concentration of 7.33 mM, and the unflooded mines at a pH of 6.68, alkalinity of 6.99 mequiv. l^{-1} and a total sulfate concentration of 3.08 mM. The model predictions for the flooded and unflooded mines are consistent with groundwater data from the study site, indicating the usefulness of this approach in evaluating the contribution of overburden chemistry to the evolution of mine discharge quality.

Keywords Geochemistry · Coalmine · Infiltration · Overburden · Pennsylvania

Introduction

Acidic discharges from abandoned coalmines are a continuing source of surface water quality degradation in many regions of the world. While many of these discharges exhibit persistent, strong acidic character, some discharges have shown improvement in quality with time (Wood and others 1999; Younger 2000; Capo and others 2001; Lambert and others 2004). A better understanding of the factors governing the chemical evolution of mine water discharges is important for improved management of abandoned coalmines and for development of restoration strategies that exploit natural amelioration processes. The chemical evolution of mine water discharge over time can be estimated by modeling geochemical interactions of water with overburden and mine void minerals encountered along the flow path. Such a model can describe mine water chemical evolution based on the dissolution and precipitation of minerals. The mineralogical characteristics of the overburden can be described using lithological models constructed from borehole logs, test pits, shaft sections and any other existing stratigraphic information. This study was part of an effort to evaluate the geochemical and hydrological factors that govern evolution in quality of abandoned underground coalmine discharges in the Uniontown syncline in southwestern Pennsylvania. Underground mining operations ceased in the 1960s after most of the Pittsburgh Coal seam in the syncline was mined out. Approximately 140 discharges were identified and monitored in 1974–1975 to assess the magnitude of the pollutant loadings to the environment and to evaluate pollution abatement measures (Ackenheil and Associates 1977). In 1998–2000, flow rates and water quality from a subset of 21 discharges were monitored to assess the extent of discharge water quality improvement relative to the 1974–1975 study (Lambert and others 2004). The aim of this study was to estimate the rate of infiltration and the chemical quality of the water that enters the abandoned Pittsburgh Coal seam mine voids in the Uniontown syncline. This was done by means of

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hydrogeologic assessments of infiltration routes and rates, and by use of geochemical modeling. A flow-through reaction-path model with kinetic and equilibrium reaction submodels was developed. Such analysis of infiltration has not been reported for abandoned mine networks, but is important for forecasting the chemical evolution of mine water. Mine discharge water quality is influenced not just by in-mine chemistry but also by the chemistry of water infiltrating from the overburden. The methodology developed in this study can be applied to estimate infiltration quantity and quality for other deep abandoned coalmines.

Tools for predicting infiltration water quality and quantity

Quality prediction with acid–base accounting

The most common and widely used approach for predicting water quality for surface mines and mine wastes is overburden rock acid–base accounting. In this approach the maximum potential acidity of the rock, based on the sulfur content, and the maximum neutralization capacity of the rock, based on the dissolution of limestone or other neutralizing rocks, are determined from chemical dissolution measurements (Sobek and others 1978). The net neutralization potential is calculated as the difference between the maximum neutralization capacity and the maximum potential acidity. A neutralization potential of 5 mg CaCO_3 per liter or higher for a rock is considered adequate to prevent release of acidic drainage from mine wastes (Sobek and others 1978). Because this approach, referred to as the Sobek test, is based on total dissolution of acid and base constituents in rock, it overpredicts the potential for acid generation and base neutralization. Further, the test is carried out under highly reactive conditions not representative of those encountered in the field. Modified versions of the Sobek test under milder reactive conditions have been proposed (Lawrence and others 1989; Coastec Research Inc. 1991). Experimental leaching tests that mimic field conditions better, e.g., use of aqueous solutions bearing weak acid, are more appropriate for accurate assessment of overburden mineral dissolution. However, the static chemical tests do not simulate the duration of solution–solid contact. The kinetics of mineral dissolution differ with each mineral (Lasaga 1984; Sherlock and others 1995), and therefore the solution–solid contact time is an important parameter to consider. Lawrence and Scheske (1997) suggested a method to calculate neutralization potential based on the mineralogy and relative reactivities of minerals. Paktunc (1999a) pointed out the shortcomings of this method and suggested that neutralization potential be calculated based on the abundance of a mineral and neutralization reaction stoichiometry (Paktunc 1999b). Paktunc (1999c) gave mineralogical constraint diagrams as guides to interpret static chemical tests to identify possible contribution of non-carbonate minerals to neutralization potential.

Geochemical approach

Although the acid–base accounting approaches can be extended to assess the chemistry of water in the rocks overlying underground mines, these approaches are primarily used in relation to mine waste piles comprising fragmented, loosely compacted rocks. The underground mining scenario is different in that the water flow is slower through the overburden due to reduced permeability of in-situ rocks. Further, mineral dissolution takes place under different conditions than in waste piles, e.g., the sequential encounter of relatively well-defined mineral layers in intact overburden. Thus, in evaluating overburden rock drainage quality for underground mines the water–rock interaction must be considered in a different manner.

A geochemical model can be used to estimate rock drainage quality with appropriate consideration of relevant reaction kinetics and equilibria. Water–rock interactions within each lithological unit of the overburden can be considered under such a framework. To model the chemical evolution of groundwater in sedimentary rocks, the order of lithological encounter must be known (Freeze and Cherry 1979). This can be established through an overburden model that gives an account of the lithology of the overburden.

In developing geochemical models for infiltration into underground mines, the water flow rates through the overburden into the mines need to be estimated. There are several factors that govern flow into abandoned mines, including the nature and permeability of the rock layers of the overburden, the extent of mining subsidence-induced fractures which in turn affect the permeability, presence of geological discontinuities, the geometry of the underground mine, and the presence of impermeable barriers that might affect subsurface flow. These features need to be considered in assessing water infiltration rates.

Fawcett and others (1984) have given a summary of mathematical models available to predict water inflow into underground mines. Models based on pumping tests (Fernandez-Rubio and Lavendiera 1983) and mechanistic models that use finite element techniques (MacLeod and others 1993) have been applied to estimate inflows into underground mines. The mathematical and mechanistic models require extensive hydrogeological data and were therefore not used in this work because the availability of geological and groundwater data was very limited. Available hydrogeological data for abandoned mine networks typically are limited.

Study site—the Uniontown syncline

The Uniontown syncline is in Fayette County, Pennsylvania (Fig. 1). The syncline is approximately 43.4 km long with the axis trending northeast–southwest. The subsurface sedimentary deposits include several coal seams, the prominent one being the Pittsburgh Coal seam with an average thickness of 2.14 m. In this study the Pittsburgh

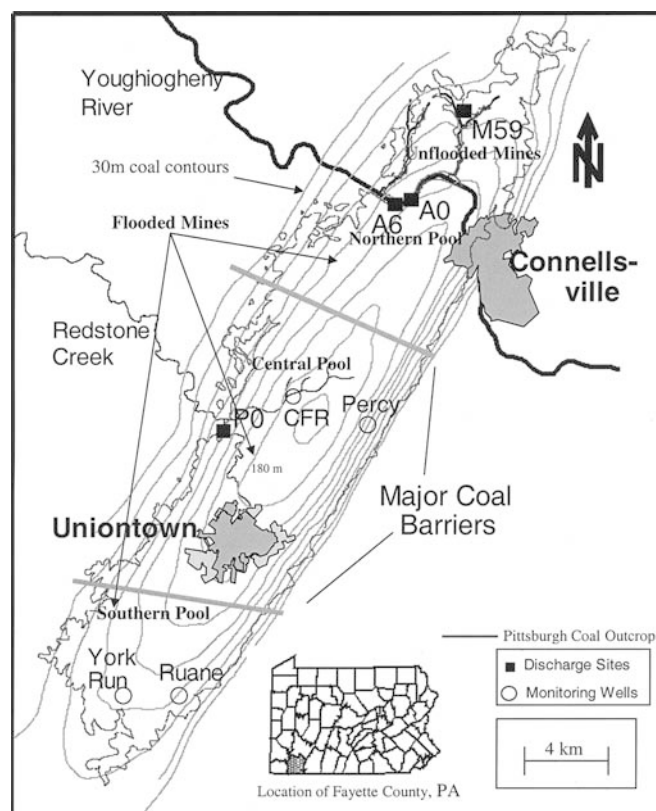


Fig. 1

Map of the Uniontown syncline showing elevation contours of Pittsburgh Coal seam (ranging from 150 m above mean sea level at the center contour to 390 m above mean sea level at the outer edge of the syncline, in 30-m increments), major in-place coal barriers and flooded mine pools south of the Youghiogheny River, mine pool monitoring well locations, and selected mine drainage discharge locations

Coal outcrop was considered to define the synclinal boundary encompassing an area of approximately 246 km². Detailed descriptions of the Uniontown syncline are given in Hickok and Moyer (1973) and Ackenheil and Associates (1977).

The network of abandoned underground mines in the Uniontown syncline encompasses flooded and unflooded mines. The mines north of the Youghiogheny River were developed updip and thus are free-draining and unflooded. The mines south of the river are flooded and the discharges from these mines are artesian. The flooded mines have further been distinguished into north, south and central mine pools (Lambert and others 2004), based on the location of mine barriers that obstruct water flow in mine voids as shown in Fig. 1.

Overburden characteristics

An overburden model was constructed for the Uniontown syncline from borehole logs, shaft sections and stratigraphic information obtained from the Pennsylvania Department of Environmental Protection, US Steel Mineral Resources, and Hickok and Moyer (1973). Figure 2 is a columnar section of Monongahela Group in which the Pittsburgh Coal seam and part of its

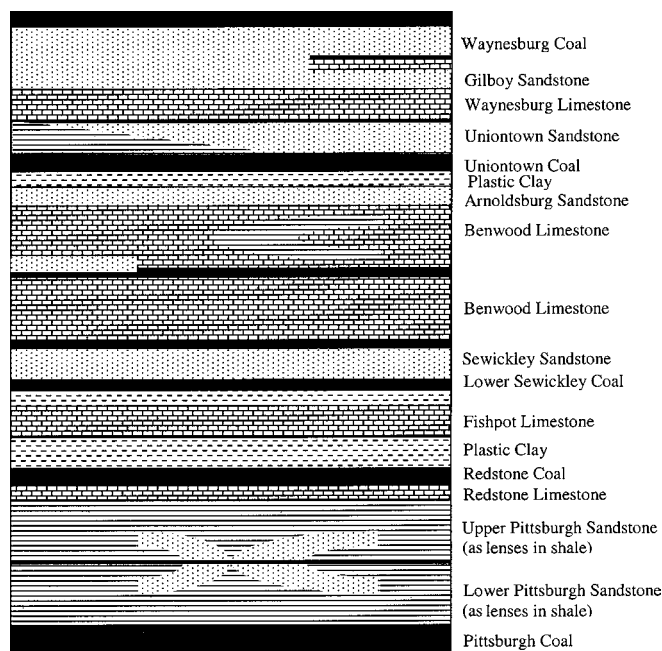


Fig. 2

Stratigraphic columnar section of Monongahela Group rocks (not to scale; adapted from Hickok and Moyer 1973)

overburden are contained. As illustrated in Fig. 2, the Pittsburgh Coal overburden consists of a series of alternating layers of shale, sandstone, limestone, clay and coal. The Monongahela Group is overlain by the Washington Group (Hickok and Moyer 1973). The two groups together form an approximately 200-m-thick cover in the central part of the Uniontown syncline. However, as will be explained below, the lithological units in the Washington Group play no role in contributing to the chemistry of water entering Pittsburgh Coal mine voids. At this stage it is pointed out that there are several clay layers in the upper regions of the Monongahela Group (Fig. 2). Further, the immediate lithological unit above the Pittsburgh Coal seam, namely, the Pittsburgh Sandstone, which occurs as bands or lenses in shale, will be shown to be a major contributor to the quality of water entering abandoned Pittsburgh Coal mines. For a detailed stratigraphic illustration of the Monongahela and Washington groups, the reader is referred to Hickok and Moyer (1973).

Zone of infiltration

The room and pillar method of mining was employed in the coalmines of the Uniontown syncline (A. Graziani, Field Inspector, US Steel Mineral Resources, Inc., Uniontown, PA, personal communication 1999). Barrier pillars were extracted on retreat, thereby allowing the immediate roof to collapse.

The subsidence of the roof of a mine will propagate through the overburden to the surface, with the magnitude of influence progressively decreasing with increase in overburden thickness. Peng (1992) has shown that four zones of mining-induced subsidence can be delineated: the caved zone in the immediate roof of the

coal seam extends from 2 to 8 times the thickness of extraction; the fractured zone above the caved zone extends from 20 to 30 times the extraction thickness; and the deformed zone extends beyond this to the surface or soil zone, as shown in Fig. 3. The fractured zone tends to dewater any aquifer that is present in it. The caved zone is highly permeable rubble that will conduct the water rapidly to the mine voids. Subsidence-induced fractures will tend to dominate over naturally occurring geological structures such as joints and faults. Further, as Hickok and Moyer (1973) observed, there are no major fault systems or joints in the Uniontown syncline.

The infiltration zones for the Uniontown syncline were identified with consideration of the importance of fracturing, and local hydrogeologic conditions. McElroy (1988) studied the quality of groundwater resources of Fayette County based on 23 test wells in the Monongahela Group which varies between 102 and 122 m in thickness. He observed that more than 90% of these test wells were dry below 30 m from surface. The fractured zone for a 2-m-thick seam, based on the subsidence discussion in Peng (1992), can be estimated to be between 60 and 75 m. Thus, subsidence fractures induced due to mining of the Pittsburgh Coal seam (2.14 m in thickness), which is at the base of the Monongahela Group, will tend to dewater any aquifer in the fracture zone which extends to nearly the upper quarter of the Monongahela Group. Confining clay layers (Fig. 2) in the upper quarter of the Monongahela Group sustain perched aquifers near the ground surface, as observed by McElroy (1988). Thus, little or no water enters from zones where overburden is thick and has upper confining layers, and these layers do not contribute

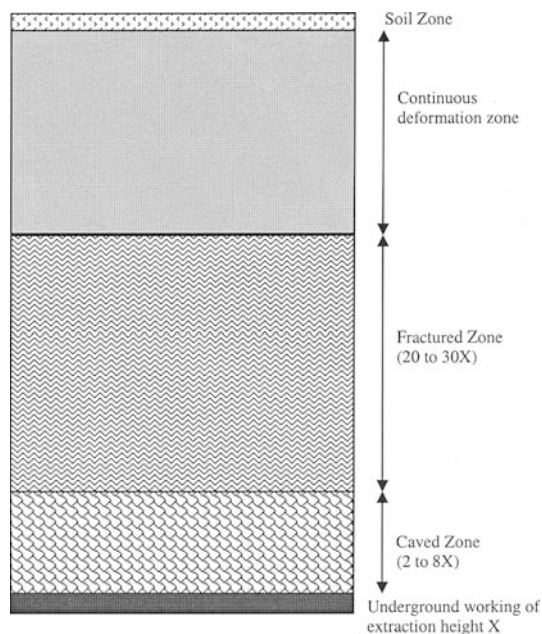


Fig. 3

Mining-induced subsidence in high-extraction (long wall and room-and-pillar) coalmines. Adapted from Peng (1992)

significantly to the quality of water entering Pittsburgh Coal mines. Therefore, it is concluded that much of the water entering the abandoned mine network of Uniontown syncline must enter near the zones where the overburden cover is shallow and severely fractured due to subsidence. This corresponds to the fringe of the Uniontown syncline where the Pittsburgh Coal seam outcrops (Fig. 4). The caved zone for the 2.14-m-thick Pittsburgh Coal seam extends approximately from 0 to 18 m above the seam and forms the major flow path to the mine voids for groundwater recharge. This zone is referred to hereafter as the zone of infiltration. Similar conclusions about the importance of shallow overburden areas for the recharge have been reached for other abandoned underground mines (Sherwood and Younger 1994).

For the flooded mines on the southern side of the Youghiogheny River in the Uniontown syncline, the shallow overburden occurs in the Pittsburgh Coal outcrop areas along the edges of the basin (Fig. 4). The overburden material in these recharge areas consists primarily of shale and sandstone (Fig. 5). The overburden for the unflooded mines north of the Youghiogheny River is typically less than 30 m thick uniformly over the entire mined areas, and not just in the vicinity of the outcrop, as in the case of the flooded mines. Consequently, the infiltration region of the unflooded mines encompasses the overburden above the entire mined area and is likely fractured over the entire area.

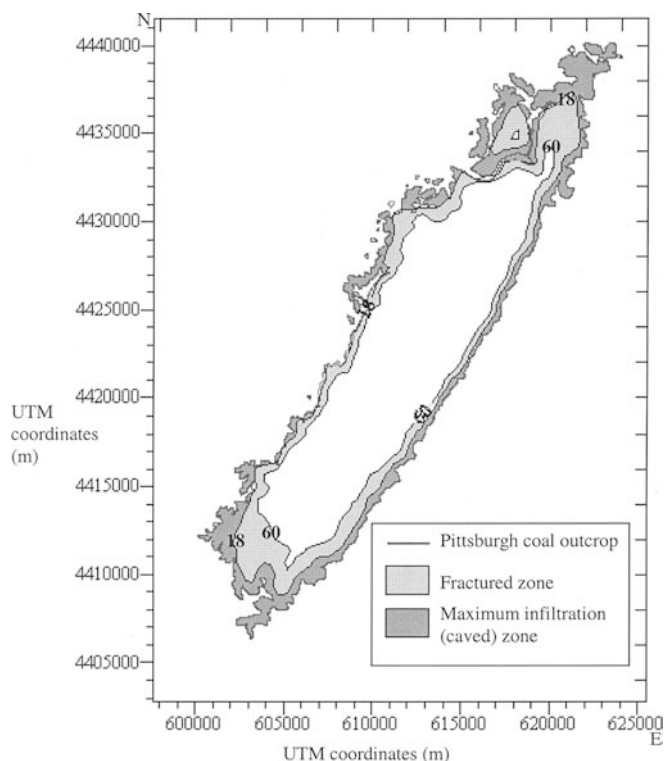
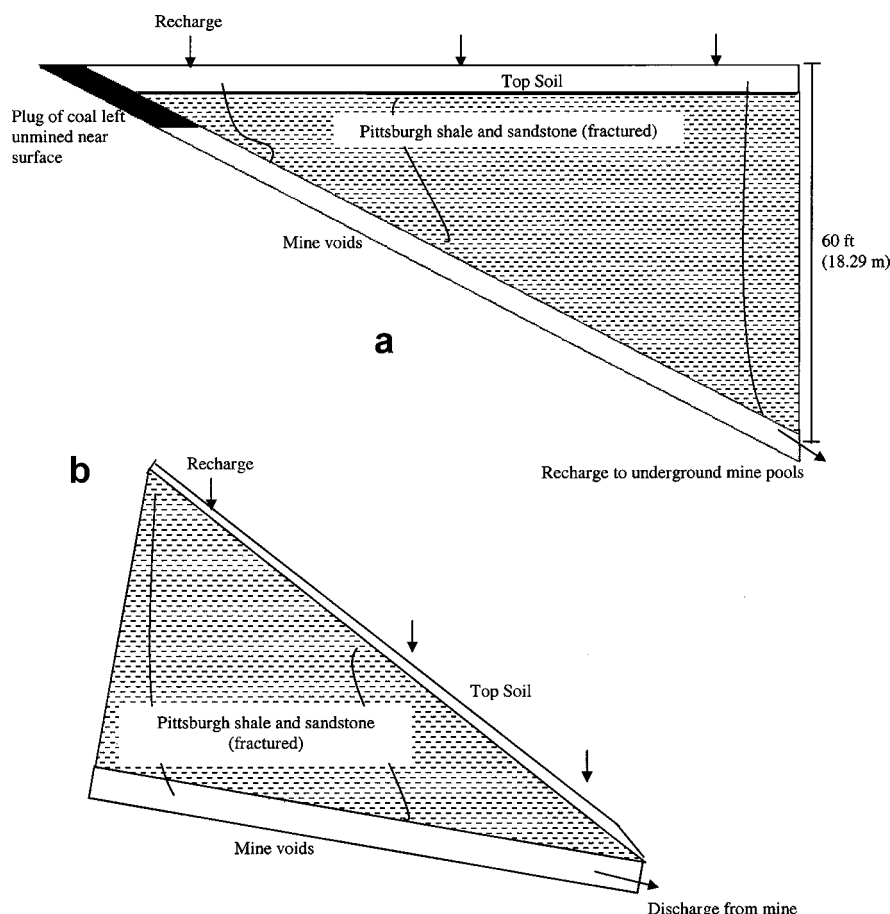


Fig. 4

Zones of infiltration, located in shallow overburden areas, for Pittsburgh Coal mine voids in the Uniontown syncline. Contours of overburden thickness of 0, 18 and 60 m are shown. Recharge occurs primarily in the areas with 0 to 18 m of overburden

**Fig. 5a, b**

Schematic diagrams of overburden in recharge areas for Pittsburgh Coal seam mine voids in the Uniontown syncline: **a** flooded mines, **b** unflooded mines

Time of solid–water contact in overburden

The solid–water contact time in the shallow overburden of the unflooded and flooded mines during infiltration is dependent on the extent of the fracturing and rock subsidence in the overburden. In the absence of direct measurement of infiltration rates, the geochemical model, which includes kinetic modeling of some dissolution reactions and equilibrium modeling of other reactions, was run with arbitrary contact times ranging from a few hours to a few years. It became evident from these simulations that the final water chemistry from the overburden evolved to similar values for contact periods greater than 5 days. This suggested that a dynamic equilibrium is achieved beyond this period, and longer contact periods do not affect the final water chemistry of the overburden drainage.

Flooded mines

The flooded mines on the southern side of the Youghiogheny River in the Uniontown syncline (Fig. 1) were considered to be at hydraulic steady state with a constant recharge rate of $0.032 \text{ m}^3 \text{ ha}^{-1}$, estimated by considering that the annual infiltration into the mine voids was equal to the annual discharge from the mine voids (Dzombak and others 2001). Aljoe (1994) used a similar approach in

estimating recharge to partially flooded mines in Pennsylvania. The recharge rate of $0.032 \text{ m}^3 \text{ ha}^{-1}$ corresponds to a seepage rate of $0.00046 \text{ m day}^{-1}$ for water in the overburden. Therefore, it would take more than five years for water to travel 9.14 m in the overburden, assuming that water infiltrates uniformly over the infiltration zone. In fractured, subsided rock, however, uniform infiltration is not likely to occur. Water is more likely to travel through preferential flow paths in the caved zone and reach the mine void system relatively quickly. As discussed above, geochemical model simulations indicated that the final water chemistry is not significantly altered for contact periods beyond 5 days. Further, the infiltration water chemistry for contact periods of 5 days or greater agreed well with the groundwater observations compiled by McElroy (1988), as shown below. Therefore, it was concluded that the water–rock contact period for the flooded mines is likely to be 5 days or greater.

Unflooded mines

The discharges from the unflooded mines north of the Youghiogheny River are generally acidic (Lambert and others 2004). However, the infiltration water with a contact period of 5 days or greater with the overburden is net alkaline. This suggests that a significant amount of the acidity is being produced in the unflooded mines. The most likely source of acidity in the mines is the dissolution of pyrite, $\text{FeS}_2(\text{s})$, which contributes to an increase in

acidity as well as the sulfate concentration (Langmuir 1997). However, the sulfate concentrations observed in the unflooded mine discharges (Lambert and others 2004) were lower than the simulated concentration of sulfate in the infiltration water. Model results indicated that sulfate concentration in the infiltration water continues to increase during the first three days of water-rock contact, and beyond this period the solubility of gypsum ($\text{CaSO}_4(\text{s})$) begins to stabilize the amount of sulfate in the system, as explained below. Reducing the contact time of water in the overburden of unflooded mines to a day or less yielded overburden sulfate concentrations low enough so that it could be augmented by sulfate production in the mine due to pyrite dissolution. This would consume the alkalinity of the infiltration water to produce a net acidic discharge, as observed in the field (Lambert and others 2004). A lower water-rock contact time for the unflooded mines is in agreement with the physical conditions for the unflooded mines. The entire infiltration area of each of the unflooded mines north of the Youghiogheny River in the Uniontown syncline is likely to be more severely fractured than the infiltration zones of the flooded mines. This is because the unflooded mines are completely mined out and there are no plugs of coal left unmined near outcrops (for prevention of water entry into mines) that provide for overburden support. Therefore, water travel through the overburden will be even more rapid for the unflooded mines and supports the interpretation of a lower contact time.

Modeling geochemical evolution of infiltration water

A geochemical model was developed for the shallow overburden in the mine recharge areas of the Uniontown syncline to gain insight into the geochemical evolution of water within the overburden, and the impact of the resulting recharge water chemistry on the mine discharge chemistry. The approach in developing this geochemical model was to track the chemical interaction of water with the rock during its downward flow, and to continuously update its chemical composition.

Models that track the geochemical evolution of a parcel of water as it traverses through the subsurface are termed flow-through reaction-path models (Bethke 1996). In a flow-through reaction-path model, minerals that precipitate out of a system are left behind and do not contribute further to the system chemistry. A flow-through equilibrium reaction-path model is based solely on local mineral equilibria, and a flow-through kinetic reaction-path model considers mineral dissolution and precipitation kinetics in tracing the geochemical evolution of a parcel of water (Bethke 1996). It is commonly necessary to combine kinetic and equilibrium models in describing a system. As explained above, most inflow to the abandoned coal-mines is through the areas of shallow overburden, which are typically close to outcrops. For the Uniontown

syncline, the lithology in these areas as determined from the overburden model can be characterized as two distinct zones: the topsoil, and the Pittsburgh Shale, which has several sandstone lenses and will be referred to as the Pittsburgh shale-sandstone unit in this paper (Fig. 5). These are the sedimentary layers above the Pittsburgh Coal in the shallow overburden areas. A flow-through equilibrium reaction-path model was applied to the topsoil unit, and the shale-sandstone unit was modeled with a flow-through kinetic-equilibrium reaction-path model as explained below.

Topsoil unit

The precipitation water that enters the ground in recharge areas for the mine voids in the Uniontown syncline first encounters a topsoil unit and then flows into a shale-sandstone unit. Water infiltrates at an average constant rate of $0.032 \text{ m}^3 \text{ ha}^{-1}$ over the infiltration area through the soil unit, as determined from a steady-state water balance (Dzombak and others 2001).

Freeze and Cherry (1979) suggest that water in an unsaturated soil zone can become saturated with calcite ($\text{CaCO}_3(\text{s})$) even for calcite quantities as low as 0.01% by weight of the soil matrix. The Monongahela Group is abundant in calcite-bearing rocks (Hickok and Moyer 1973; Brady and others 1998). Therefore, the topsoil was considered to contain amounts of calcite sufficient to saturate the water with Ca^{2+} . The calcite dissolution was considered to take place under open system conditions in the soil atmosphere. The amount of calcite that dissolves will depend on the partial pressure of soil carbon dioxide. In soil, CO_2 is primarily of biogenic origin. Trainer and Heath (1976) demonstrated that CO_2 content in soil atmospheres in temperate conditions is high, typically 1% or higher. They identified typical values during the growing and non-growing seasons as 3.04 and 1.01 kPa, respectively. For the topsoil unit in the Uniontown syncline recharge areas, a mean value of 2.03 kPa was used. It was also assumed that calcite dissolution is the dominant reaction affecting acid-base chemistry in the soil zone. Calcite dissolution is relatively rapid. Using the rate law of Plummer and others (1979), and from the discussion in Langmuir (1997), it may be concluded that calcite can saturate water with respect to Ca^{2+} in minutes. Thus, for a soil-water contact period in the order of hours or days, it can be assumed that water reaches equilibrium with soil calcite rapidly following initial soil-water contact. The topsoil unit was therefore modeled as flow-through system with the water chemistry being determined by calcite dissolution to equilibrium under open system conditions. Calcite was the only mineral considered to alter the acid-base chemistry of the water parcel in the topsoil. The chemical equilibrium problem for the soil water in the topsoil unit was calculated using MINEQL+ software (Schecher and McAvoy 1998). The calcite solubility was allowed to control the concentration of calcium in solution and the P_{CO_2} was set to 2.03 kPa. The equilibrium pH and Ca^{2+} concentration corrected for ionic strength were determined as 7.07 and 2.04 mM, respectively.

Table 1

Groundwater data from wells in Monongahela Group rocks, Fayette County, Pennsylvania^a

Parameter ^b	Conc. range (mg l ⁻¹)	Conc. range as -log C (mol l ⁻¹)	Aver. (mg l ⁻¹)	Aver. as -log C (mol l ⁻¹)
H ⁺	n.a. ^c	7.0–6.7	n.a.	6.9
Na _(T,diss)	13.6–107.3	3.23–2.33	57.6	2.60
K _(T,diss)	1.56–6.62	4.40–3.77	3.34	4.07
Ca _(T,diss)	51.1–415	2.89–1.98	187	2.33
Mg _(T,diss)	18.3–60.8	3.12–2.60	39.9	2.78
Cl _(T,diss)	4–352	3.95–2.00	94	2.58
SO _{4(T,diss)}	50–1,200	3.28–1.90	376	2.41
Al _(T,diss)	0.06–0.08	5.65–5.53	0.07	5.59
Fe _(T,diss)	0.14–4.25	5.60–4.12	2.24	4.40
Alk.	286–350 ^d	2.24–2.15 ^e	304	2.21 ^f
TDS ^g	378–1,930	n.a.	1,081	n.a.

^aSource: McElroy (1988), page 45, Table 12. Data based on results from four wells

^bDissolved concentrations reported for all parameters; T,diss, total dissolved

^cn.a., not applicable

^dMass concentration expressed as CaCO₃

^eWith C expressed in equiv. l⁻¹; range corresponds to 5.72–7.00 mequiv. l⁻¹

^fWith C expressed in equiv. l⁻¹; average corresponds to 6.08 mequiv. l⁻¹

^gTDS, total dissolved solids

Pittsburgh shale–sandstone unit

The Pittsburgh shale–sandstone unit immediately above the Pittsburgh Coal seam (Figs. 2 and 5) contains finely distributed, sedimentary pyrite as determined by chemical tests on overburden cores (Garbert Consulting Inc. 2000, Lemont Furnace, PA, unpublished data). In addition, Brady and others (1998) point out that there is a significant quantity of calcareous material in Monongahela shales and sandstones. This is confirmed by the positive neutralization potential for the shale–sandstone unit, as determined in acid–base accounting tests on the overburden cores (Garbert Consulting Inc. 2000, Lemont Furnace, PA, unpublished data).

Water samples from the wells in the Monongahela Group (McElroy 1988) indicate the presence of sodium and magnesium in addition to calcium, as shown in Table 1. The discharge water quality monitored during this study (Lambert and others 2004) also indicates the presence of these ions in significant concentrations. Dolomite (CaMg(CO₃)₂(s)) is the likely source of magnesium, given the calcareous nature of these rocks. Based on a strontium isotopic tracer study, Capo and others (2001) have suggested that calcium cation exchange in clay and shale is a dominant source of sodium in coalmine drainage.

The water–rock interaction in the shale–sandstone unit was assumed to involve primarily pyrite dissolution that contributes acidity, and calcite and dolomite dissolution that neutralizes the acidity. Further, the fractures in the overburden were assumed to create open system conditions in the subsurface atmosphere, thus providing a continuous supply of oxygen for pyrite dissolution. The rate of pyrite dissolution is slow in contrast to calcite dissolution (Langmuir 1997). Therefore, the flow-through kinetic-equilibrium reaction-path model for the shale–sandstone unit included kinetic dissolution of pyrite and equilibration of the resulting water with calcite and dolomite. Any solids predicted to form (gypsum and siderite, FeCO₃(s)) were considered to be deposited in the shale–sandstone unit.

The kinetics of pyrite dissolution depend on the dissolved oxygen concentration and the pH at which the dissolution takes place (McKibben and Barnes 1986; Nicholson and others 1988; Paschka 2001). The reaction is faster at higher pH and slows as pH decreases. The dissolution of pyrite was considered to occur via oxidation with oxygen, with open system conditions for oxygen re-supply facilitated by subsidence-induced fracturing of the rock. Further, it was assumed that the dissolution was abiotic and that oxygen was the only electron acceptor. The rate laws for abiotic pyrite dissolution in different pH ranges given by McKibben and Barnes (1986), Nicholson and others (1988), and Paschka (2001), shown in Table 2, were used in the model.

Chemical data compiled by McElroy (1988) for groundwater from wells in the calcareous Monongahela Group rocks, summarized in Table 1, indicate a pH range of 6.7–7.0 and alkalinity of 286–350 mg l⁻¹ as CaCO₃ (5.7–7.0 mequiv. l⁻¹). These data imply a partial pressure of CO₂ (P_{CO2}) of 3.5–9.3 kPa. Similar alkalinity and calculated P_{CO2} values have been reported by others for groundwaters contacted with carbonate-bearing rocks (Hem 1985; Hedin and others 1994). Further, the mine drainage discharges monitored for the Uniontown syncline exhibited comparable dissolved inorganic carbon concentrations (Lambert and others 2004). Therefore, for the assumed open system conditions, P_{CO2} was set at 7.3 kPa, the mid-range value of the data for the Monongahela Group wells compiled by McElroy (1988).

The chemical reactions considered for the Pittsburgh shale–sandstone overburden unit are summarized in Table 3. The corresponding mass balance and mass action equations are given in Table 4. The first reaction listed in Table 3 is kinetically controlled and the other reactions are at equilibrium. Aqueous phase hydroxide species of Ca²⁺, Mg²⁺, and Fe²⁺ were neglected as these species become

Table 2

Rate laws for abiotic pyrite dissolution

Source	Rate law	pH
McKibben and Barnes (1986)	Rate=10 ^{-6.77} [O ₂] ^{0.5} mol pyrite cm ⁻² min ⁻¹	<3
Paschka (2001)	Rate=10 ^{-7.5} [H ⁺] ^{0.43} [O ₂] ^{0.5} mol pyrite l ⁻¹ min ⁻¹	3–6
Nicholson and others (1988)	Rate=5.05×10 ⁻⁸ ×1,360[O ₂]/(1+1,360[O ₂]) mol pyrite s ⁻¹ g ⁻¹	>6

Table 3

Chemical reactions in the shale-sandstone unit

Reaction	
Kinetically controlled reaction	
$\text{FeS}_2(\text{s}) + 7/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$	
Equilibrium reactions	
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$\log K^a$
$\text{CaCO}_3(\text{s}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-14.00 ^b
$\text{CaMg}(\text{CO}_3)_2(\text{s}) = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-8.34 ^b
$\text{H}_2\text{O} + \text{CO}_2(\text{g}) = \text{H}_2\text{CO}_3^*$	-17.00 ^c
$\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$	-1.46 (K_H)
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	-6.35 ^c
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$	-10.28 ^c
$\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_4^0$	2.31 ^b
$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3(\text{s})$	2.25 ^c
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4(\text{s})$	10.70 ^b
	4.62 ^b

^aValues of stability constants at 25 °C and zero ionic strength^bValues from Morel and Hering (1993)^cValues obtained from MINEQL+ (Schecher and McAvoy 1998) database**Table 4**

Mass law and mole balance equations for chemical reactions in the shale-sandstone unit

Equation

Mass law equations^a

$$\{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}=10^{-8.34}$$

$$\{\text{Mg}\}\{\text{CO}_3^{2-}\}=10^{-8.66}$$

$$\{\text{MgSO}_4\}/\{\text{Mg}^{2+}\}\{\text{SO}_4^{2-}\}=10^{-2.25}$$

$$\{\text{CaSO}_4\}/\{\text{Ca}^{2+}\}\{\text{SO}_4^{2-}\}=10^{-2.31}$$

$$\{\text{CO}_3^{2-}\}\{\text{H}^+\}^2/P_{\text{CO}_2}=10^{-18.09}$$

$$\{\text{HCO}_3^-\}\{\text{H}^+\}/P_{\text{CO}_2}=10^{-7.41}$$

$$\{\text{Ca}^{2+}\}\{\text{SO}_4^{2-}\}=10^{-4.62}$$

$$\{\text{Fe}^{2+}\}\{\text{CO}_3^{2-}\}=10^{-10.7}$$

Mole balance equations^b

$$[\text{SO}_4^{2-}]_{(\text{T,diss})}=[\text{SO}_4^{2-}]+[\text{CaSO}_4]+[\text{MgSO}_4]$$

$$[\text{H}]_{(\text{T,diss})}=[\text{H}^+]-[\text{OH}^-]-[\text{HCO}_3^-]-2[\text{CO}_3^{2-}]$$

$$=2[\text{SO}_4^{2-}]+[\text{Cl}^-]-2[\text{Ca}^{2+}]-2[\text{Mg}^{2+}]-[\text{Na}^+]$$

$$[\text{Ca}^{2+}]_{(\text{T,diss})}=[\text{Ca}^{2+}]+[\text{CaSO}_4]$$

$$[\text{Mg}^{2+}]_{(\text{T,diss})}=[\text{Mg}^{2+}]+[\text{MgSO}_4]$$

$$[\text{CO}_3^{2-}]_{(\text{T,diss})}=[\text{H}_2\text{CO}_3^*]+[\text{HCO}_3^-]+[\text{CO}_3^{2-}]$$

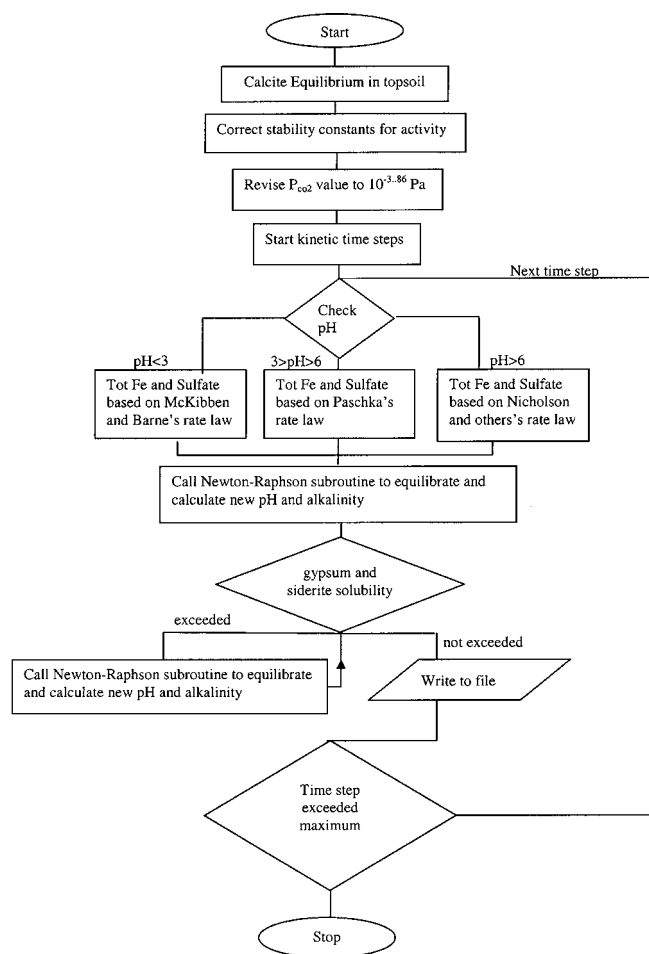
$$[\text{Fe}^{2+}]_{(\text{T,diss})}=[\text{Fe}^{2+}]$$

$$[\text{Na}^+]_{(\text{T,diss})}=[\text{Na}^+]$$

$$[\text{Cl}^-]_{(\text{T,diss})}=[\text{Cl}^-]$$

^a{ } represent species activity; calculations were conducted with correction for ionic strength^b[] represent species molar concentration; T, diss, total dissolved

important only at higher pH values. The concentrations of these species are several orders of magnitude lower than the free ions at circumneutral or low pH that is typically the case for mine infiltration waters in the Uniontown syncline. For the shale-sandstone geochemical model, P_{CO_2} was set at 7.3 kPa and the dissolved oxygen for pyrite dissolution was kept constant at 8.0 mg l⁻¹. A water-rock contact period of 5 days in the overburden was assumed for the flooded mines. Assuming a uniform

**Fig. 6**

Algorithm for reaction-path geochemical model used to predict infiltration water quality for Pittsburgh Coal mine voids in the Uniontown syncline

infiltration rate through an average thickness of 9.14 m of overburden, including 0.91 m of topsoil and 8.23 m of shale-sandstone, the time of contact with the shale-sandstone unit was 4.5 days. For the unflooded mines the water-rock contact time was set to 24 h, with 2.4 h in the topsoil and 21.6 h in the shale-sandstone unit. Each kinetically controlled pyrite dissolution time step (dt) was set to last for an hour in the flooded model simulations and 30 min in the unflooded model simulations, and the amount of pyrite dissolving in each such step was calculated by using an Eulerian solution to the appropriate differential equation (Table 2). The equilibration was assumed to be instantaneous. Therefore, for 4.5 days a total of 108 kinetic-equilibrium time steps were executed for the flooded mine infiltration simulations and 48 time steps were considered for the unflooded mines. A C++ code (Dzombak and others 2001) was written to solve the pyrite dissolution and equilibrium model equations for each time step. The computational scheme for the reaction-path geochemical model is illustrated in the flowchart in Fig. 6. Depending on the pH at each time step, one of the three abiotic pyrite dissolution rate laws given in Table 2 was used to

Table 5

Simulated overburden discharge (mine void infiltration) water quality for recharge areas of the Uniontown syncline

Parameter	Infiltration constituent concentrations (mol l ⁻¹) -log C ^a	
	Flooded mines	Unflooded mines
H ⁺	6.65	6.68
O ₂ (aq)	3.60	3.60
SO ₄ ²⁻	2.26	2.65
Ca ²⁺	2.36	2.41
Mg ²⁺	2.68	2.73
Na ⁺	2.27	3.70
Fe(II) _T ^b	5.30	5.22
CaSO ₄ (aq)	2.88	3.23
MgSO ₄ (aq)	3.26	3.61
Alk. ^c	2.16	2.16
Ca(T,diss)	2.24	2.35
SO ₄ (T,diss)	2.13	2.51
Mg(T,diss)	2.57	2.68
CO ₃ (T,diss)	2.03	2.02

^aDissolved concentrations given for all constituents, with C expressed in mol l⁻¹; T,diss, total dissolved

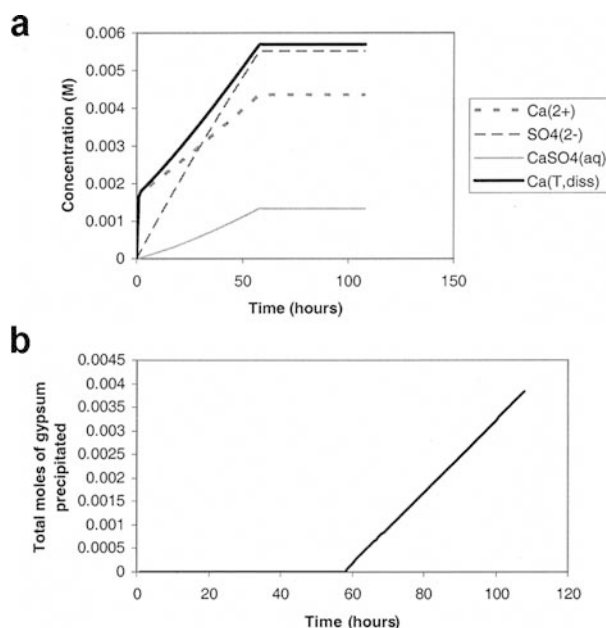
^bFe(II)_T represents the total dissolved concentration of ferrous iron. The hydroxy species of ferrous iron are negligible for the pH range of interest and hence Fe(II)_T is equivalent to the dissolved Fe²⁺ concentration

^cFor alkalinity, C expressed in equiv. l⁻¹

calculate the sulfate and iron entry into the system. Sodium was allowed to enter the system at a uniform rate of 4.42×10^{-5} mol l⁻¹ h⁻¹ (source unspecified) to make up the final concentration of 0.053 mol l⁻¹ observed in the discharges (Lambert and others 2004). The equilibrium model was used to calculate the pH and the aqueous phase speciation upon equilibration. In each iteration the system was allowed to precipitate solids (gypsum and siderite) if the solubility products were exceeded, and repeated equilibrium calculations were performed until the saturation index fell below unity. The precipitated solids were considered to exit the system and were not allowed to reenter.

Results and insights

The results for the overburden discharge (mine water recharge) water quality predicted with the flow-through kinetic-equilibrium reaction-path model in the shale-sandstone unit are summarized in Table 5. Both calcium and magnesium form dissolved complexes with sulfate that become significant with increased sulfate concentrations. The sulfate in the discharges was predicted to be more than 30% complexed with calcium and magnesium. As more sulfate enters the system due to pyrite dissolution, the free sulfate concentration can become high enough that gypsum precipitates. Calcite and dolomite in turn dissolve to compensate for the loss of calcium from the system. Over a period of time the various reaction processes—the dissolution of pyrite, the neutralization by calcite and dolomite, and the removal of sulfate as

**Fig. 7a, b**

Predicted changes in **a** concentration of dissolved calcium and sulfate species, and **b** total moles of gypsum precipitated in mine recharge water as a function of time

gypsum—reach a dynamic equilibrium to keep a nearly constant concentration of ions in solution. Figure 7a illustrates the change in the solution concentrations of calcium and sulfate ions in the mine water recharge. Figure 7b shows the total amount of gypsum precipitated once the concentrations of Ca²⁺ and SO₄²⁻ are high enough to exceed gypsum solubility. Siderite provides a removal mechanism for ferrous iron. The concentration of carbonate determines the pH of the system and this in turn determines the amount of iron that can stay in solution. Complexation of Fe²⁺ with OH⁻, Cl⁻, and SO₄²⁻ was ignored to simplify the calculations. At circumneutral and acidic pH, the concentrations of these species are low for typical anion concentrations, and free Fe²⁺ will be the dominant ferrous species. (It was verified, through equilibrium modeling with all species considered, that this assumption did not significantly affect the final pH, alkalinity, and solution concentrations of calcium, magnesium, sulfate, and carbonate.) The total ferrous iron concentrations predicted, in the range 10^{-5.3}–10^{-5.2} M, were in the range of field observations for total dissolved iron, which spanned 10^{-4.1}–10^{-5.6} M (Table 1).

As indicated in Table 5, the model predicted water entering the flooded mines at a pH of 6.65, alkalinity of 10^{-2.16} N (6.92 mequiv. l⁻¹), total sulfate of 10^{-2.135} M (7.33 mM), and total calcium of 10^{-2.24} M (5.75 mM), and for the unflooded mines at a pH of 6.68, alkalinity of 10^{-2.155} N (6.99 mequiv. l⁻¹), total sulfate of 10^{-2.51} M (3.08 mM), and total calcium of 10^{-2.35} M (4.47 mM). The model predictions are comparable to the groundwater observations for the Monongahela Group compiled by McElroy (1988) and given in Table 1.

The geochemical model could be improved by considering dissolution of other neutralizing materials such as

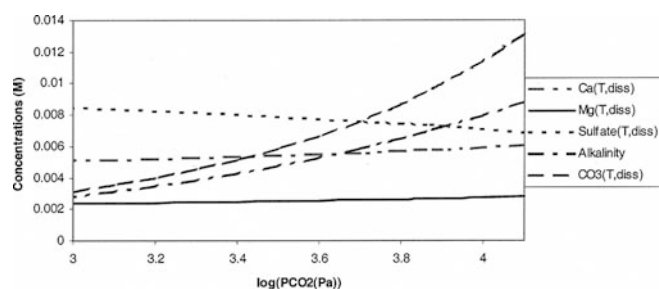


Fig. 8

Influence of P_{CO_2} on total dissolved concentrations in the shale-sandstone unit as calculated with the flow-through kinetic-equilibrium reaction-path model

silicates. Also, a biogeochemical model considering the effects of microbiological activity in addition to water-rock interaction chemistry would provide added insight into the water quality evolution of overburden rock drainage.

Sensitivity of reaction-path model to P_{CO_2}

In the flow-through, kinetic-equilibrium reaction-path model, the partial pressure of CO_2 in the overburden controls the amount of calcium and magnesium that comes into the system through calcite and dolomite dissolution. This, in turn, controls the bicarbonate alkalinity and the pH of the system and the ability of the system to neutralize the acid produced due to pyrite dissolution. The sensitivity of the model to partial pressures of CO_2 was examined. The P_{CO_2} was varied from 12.8 to 1.0 kPa. The sensitivity of the aqueous species concentrations to P_{CO_2} is shown in Fig. 8 and the change in pH is shown in Fig. 9. It can be seen that a high P_{CO_2} brings a high alkalinity into the system through elevated concentrations of calcium and magnesium. The higher concentrations of calcium and magnesium cause a higher removal of sulfate as gypsum, thereby reducing total sulfate concentration in the system. It can also be noted from Fig. 9 that pH decreases linearly with increase in P_{CO_2} due to increased CO_2 acidity in the system. The average total dissolved inorganic carbon measured for the two largest discharges from the flooded mines of the Uniontown syncline were 0.0136 and 0.0195 M, respectively (Lambert and others 2004). As there are no significant sources of CO_2 in the mine besides autooxidation of coal, the overburden is likely to be the main contributor to the dissolved inorganic carbon in the discharges. This suggests that P_{CO_2} is perhaps even higher than the 7.3 kPa used in the model.

Summary and conclusions

The evolution of abandoned mine discharge water quality depends on mine void infiltration water chemistry as well as in-mine chemistry. Modeling of discharge water quality from abandoned mines thus must consider the contribution from the overburden. Estimation of infiltration water quality to abandoned coalmines can be done via

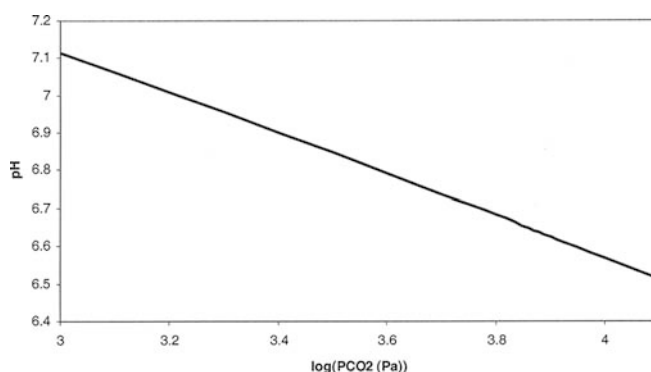


Fig. 9

Change in pH with P_{CO_2} for the shale-sandstone unit as calculated with the flow-through kinetic-equilibrium reaction-path model

geochemical modeling. Infiltration through the rocks overlying the Pittsburgh Coal seam in the Uniontown syncline, Fayette County, Pennsylvania was used as an example to demonstrate the usefulness of such an approach. From consideration of local hydrogeologic conditions coupled with existing knowledge of fracturing above abandoned coalmine voids due to subsidence and the importance of such fracturing in water recharge, it was concluded that most recharge to the mine voids in the Uniontown syncline occurs in shallow overburden areas less than 20 m in thickness. For the flooded mines that are developed to depths of up to 200 m in the Uniontown syncline, the shallow overburden and recharge areas are in the vicinity of the coal outcrops. For the unflooded mines with shallow overburden, the entire area of the overburden likely contributes to recharge. The geochemistry of the zone of overburden through which most of the recharge to the underground mine pool takes place determines the chemical evolution of water in the overburden, and influences the quality of the mine drainage to lesser and greater extents, depending on in-mine conditions. For the evaluation of mine void infiltration water quality in the Uniontown syncline, the overburden in the recharge areas was defined as a thin topsoil layer over a layer of shale-sandstone up to 18 m in thickness. A flow-through kinetic-equilibrium reaction-path geochemical model was used to evaluate infiltration water chemistry. Dissolution of calcite to equilibrium under open system conditions was considered for the topsoil unit. Rate-limited dissolution of pyrite followed by equilibration with calcite and dolomite was considered for the shale-sandstone unit. The shale-sandstone unit was considered to be highly fractured and to thus function as an open system. Model results were sensitive to P_{CO_2} ; the P_{CO_2} values used for the topsoil and shale-sandstone were consistent with values reported for similar environments. The model predicted water entering the flooded mines at a pH of 6.65, alkalinity of 6.92 mequiv. l^{-1} and total sulfate of 7.33 mM, and the unflooded mines at a pH of 6.68, alkalinity of 6.99 mequiv. l^{-1} and a total sulfate of 3.08 mM. The results are consistent with groundwater data from the study site (McElroy 1988). These results suggest that there is a substantial amount of alkalinity coming into the underground

mine pools from the overburden, which contributes, along with other in-mine factors such as extent of flooding (which governs oxygen availability) and pyrite availability, to the ultimate mine discharge water quality.

The geochemical approach can be extended to active surface and underground mines. It can be customized to any set of complex geochemical conditions by discretizing the overburden into individual units and keeping track of the chemistry in each unit. If sufficient lithological and geochemical data are available, the modeler can capture important water–rock interactions, which will improve model accuracy and usefulness for designing mine water handling and treatment systems. This approach can also be used to identify acidic overburdens and plan strategies for designing naturally ameliorating overburden spoil dumps.

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References

- Ackenheil and Associates (1977) Acid mine drainage abatement survey, Redstone Creek watershed and the Uniontown syncline. Department of Environmental Resources, Commonwealth of Pennsylvania, Harrisburg, PA, Operation Scarlift Rep SL 141-2
- Aljoe WW (1994) Hydrological and water quality characteristics of a partially flooded, abandoned underground coal mine. In: *Proc Int Land Reclamation and Mine Drainage Conf, 3rd Int Conf Acidic Drainage*, Pittsburgh, PA, vol 2. US Bureau Mines Spec Publ 06B-94, pp 178–187
- Bethke CM (1996) *Geochemical reaction modeling*. Oxford University Press, New York, pp 18–20, 169, 170, 214, 215
- Brady KBC, Hornberger RJ, Fleeger G (1998) Influence of geology on postmining water quality: Northern Appalachian Basin. In: Brady KBC, Smith MW, Schueck J (eds) *Coal Mine drainage prediction and pollution prevention in Pennsylvania*. Pennsylvania Department of Environmental Protection, Harrisburg, PA, pp 8-3–8-6, 8-23–8-26
- Capo RC, Winters RW, Weaver TJ, Stafford SL, Hedin RS, Stewart BW (2001) Hydrogeological and geochemical evolution of deep mine discharges, Irwin syncline, Pennsylvania. In: Miller C (ed) *Proc 22nd West Virginia Surface Mine Drainage Task Force Symp*, National Mine Land Reclamation Center, Morgantown, WV, pp144–153
- Coastec Research Inc (1991) Acid rock drainage prediction manual. Report prepared for CANMET under MEND Proj no 1.16.1(b), Department of Energy, Mines and Resources, Canada
- Dzombak DA, McDonough KM, Lambert DC, Mugunthan P (2001) Evaluation of natural amelioration of acidic deep mine discharges for watershed restoration. Final Rep US Environmental Protection Agency, National Center for Environment Research, Washington, DC. Available at NCER website <http://es.epa.gov/ncer/publications/>
- Fawcett RJ, Hibberd S, Singh RN (1984) An appraisal of mathematical models to predict water inflows into underground coal workings. *Int J Mine Water* 3(2):33–54
- Fernandez-Rubio R, Lavendiera A (1983) Hydrogeological investigations and drainage infrastructure at underground zinc and lead Troya mine. *Int J Mine Water* 2(3):39–56
- Freeze RA, Cherry JA (1979) *Groundwater*. Prentice-Hall, Upper Saddle River, NJ, pp 63–74, 254–256, 280–284
- Hedin RS, Watzlaf GR, Nairn RW (1994) Passive treatment of acid mine drainage with limestone. *J Environ Quality* 23:1338–1345
- Hem JD (1985) *Study and interpretation of chemical characteristics of natural water*, 3rd edn. US Geological Survey, Alexandria, VA, US Geol Surv Water-Supply Pap 2254, pp 106–109
- Hickok WO, Moyer FT (1973) *Geology and mineral resources of Fayette County, Pennsylvania*. Pennsylvania Geological Survey, Harrisburg, PA, pp 100–134
- Lambert DC, McDonough KM, Dzombak DA (2004) Long-term changes in quality of discharge water from abandoned underground coal mines in Uniontown syncline, Fayette County, Pennsylvania, USA. *Water Res* 38:277–288
- Langmuir D (1997) *Aqueous environmental geochemistry*. Prentice Hall, Upper Saddle River, NJ, pp 73–74
- Lasaga AC (1984) Chemical kinetics of water-rock interactions. *J Geophys Res* 89:4009–4025
- Lawrence RW, Scheske M (1997) A method to calculate the neutralization potential of mining wastes. *Environ Geol* 32(2):100–106
- Lawrence RW, Poling GP, Marchant PB (1989) Investigations of predictive techniques for acid mine drainage. Report on DSS Contract no 23440-7-9178/01-SQ, Energy Mines and Resources, Canada MEND Rep 1.16.1(a)
- MacLeod R, Bursey GG, Aston TRC, Gale JE (1993) Preliminary modeling of groundwater inflows at Gays River Mine, Nova Scotia, Canada. *Trans Inst Mining Metall Sect A Min Industry* 102:A153–A164
- McElroy TA (1988) *Groundwater resources of Fayette County, Pennsylvania*. Pennsylvania Geological Survey, Harrisburg, PA, Water Resource Rep 60
- McKibben MA, Barnes HL (1986) Oxidation of pyrite in low temperature acidic solutions: rate laws and surface textures. *Geochim Cosmochim Acta* 50:1509–1520
- Morel FMM, Hering JG (1993) *Principles and applications of aquatic chemistry*. Wiley, New York, NY, pp 332–334
- Nicholson RV, Gillham RW, Reardon EJ (1988) Pyrite oxidation in carbonate-buffered solutions. 1. Experimental kinetics. *Geochim Cosmochim Acta* 52:1077–1085
- Paktunc AD (1999a) Discussion of a method to calculate the neutralization potential of mining wastes. *Environ Geol* 38(1):82–84
- Paktunc AD (1999b) Characterization of mine wastes in prediction of acid mine drainage. In: Azcuez JM (ed) *Environmental impacts of mining activities*. Springer, Berlin Heidelberg New York
- Paktunc AD (1999c) Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. *Environ Geol* 39(2):103–112
- Paschka M (2001) Kinetics of pyrite oxidation. MSc Thesis, Carnegie Mellon University, Pittsburgh, PA
- Peng SS (1992) *Surface subsidence engineering*. Society of Mining, Metallurgy and Exploration Inc, Littleton, CO, pp 1–8
- Plummer LN, Parkhurst DL, Wigley TML (1979) Critical review of kinetics of calcite dissolution and precipitation. In: Jenne EA (ed) *Chemical modeling of aqueous systems*. American Chemical Society, Washington, DC, ACS Symp Series 93, pp 537–573

- Schecher WD, McAvoy DC (1998) MINEQL+: chemical equilibrium modeling system, version 4.07. Environmental Research Software, Hallowell, ME
- Sherlock EJ, Lawrence RW, Poulin P (1995) On the neutralization of acid rock drainage by carbonate and silicate minerals. *Environ Geol* 25:43–55
- Sherwood JM, Younger PL (1994) Modeling groundwater rebound in coalfield closure: an example from County Durham, UK. In: Reddish DJ (ed) *Proc 5th Int Mine Water Congr*, Nottingham, UK. University of Nottingham, vol 2, pp 769–777
- Sobek AA, Schuller WA, Freeman JR, Smith RM (1978) Field and laboratory methods applicable to overburdens and minesoils. Industrial Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH, EPA-600/2-78-054
- Trainer FW, Heath RC (1976) Bicarbonate content of groundwater in carbonate rock in eastern north America. *J Hydrol* 31:37–55
- Wood SC, Younger PL, Robins NS (1999) Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland. *Q J Eng Geol Hydrogeol* 32(1):69–79
- Younger PL (2000) Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *J. Contam Hydrol* 44:47–69